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Treatment of titanium white waste acid using ceramic microfiltration membrane

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Abstract

The aim of the research was to study the clarification of titanium white waste acid by ceramic microfiltration membrane. The main focus was the effect of high concentration $FeSO_4$ and flocculant of polyacrylamide (PAA) on the filtration. The influence of operating parameters such as transmembrane pressure, cross-flow velocity, concentration and temperature on filtration process was also investigated. The results showed that hydrated TiO_2 in waste acid can be successfully recovered by ceramic membrane microfiltration and an excellent clarification effect was achieved. The high concentration of $FeSO_4$ in waste acid complicates the effect of temperature on the filtration process. When the temperature decreased to less than 293 K, crystallization of $FeSO_4$ may occur in the membrane pores, hence it is difficult to regenerate the membrane. Flocculation by modified PAA, of which the concentration was less than 5 ppm, slightly increased the membrane flux. Further addition of flocculants might cause adsorption fouling of the membrane and resulted in decrease of flux. The membrane flux was also affected by other parameters. Analyses of filtration resistances indicated that the cake resistance was the main component of the fouling resistance and was 68–80% of the total resistance. The analyses gave more quantitative understanding into the effects of the operating parameters on the filtration.

Keywords: Ceramic membrane; Microfiltration; Titanium white waste acid; Clarification; Operating parameters

1. Introduction

Large quantities of spent acid are produced from the sulfuric acid process in TiO_2 plants. In addition to containing more than 20% free H_2SO_4, the waste acid contains 1–2% hydrated TiO_2 suspension, 8% $FeSO_4$ and other metal ions. Disposal of this liquor not only pollutes the environment but also causes the loss of economic benefits. Diffusion dialysis, which is driven by the difference in the diffusivity between acids and salts, appeals to be an attractive acid recovery method from the viewpoint of energy saving [1–3]. However, removal of the hydrated TiO_2 particles before diffusion dialysis is necessary to prevent serious fouling of the anion exchange membrane by the particles, which in turn influences the dialysis efficiency. On the other hand, recovery of the hydrated TiO_2 particle is also important because it is closely related to the yield of TiO_2.

Many plants have attempted to recover the hydrated TiO_2 particles from the waste acid using conventional gravity settling; however, this method requires a long residence time and a large floor space, yet performs poorly [4,5]. Porous tube filtration is also used to recover these particles, but porous tubes are easily plugged and difficult to clean [6]. Microfiltration (MF) and ultrafiltration (UF) have emerged as useful processes for concentrating fine particles and clarifying wastewater. Most polymeric MF/UF membranes, however, cannot be used to recover TiO_2 particles from such waste acid due to the material nature of the membrane. Ceramic MF/UF membranes have inherently superior physical integrity, chemical resistance, and thermal stability

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[7]. These advantages rendered them suitable for extreme-condition applications. Several researchers have investigated the use of ceramic MF membranes for treating wastewater containing micron and submicron particles [8–11]. Most of these applications achieved permeate flux ranging from 100 to 300 L m^{-2} h^{-1}, when operated at a cross-flow velocity of 3–4 m s^{-1}, a transmembrane pressure of 3.5 bar, and/or an operating temperature of 20–90 °C. Our previous works also showed that ceramic microfiltration is a proper technology to recover the TiO_2 particles in acid wastewater [12,13] and rinse wastewater [14] produced from different processes in the TiO_2 plants. As far as the waste acid is concerned, however, high concentrations of $FeSO_4$ and flocculant (PAA) may affect the filtration behaviour of ceramic membranes. To date, there has been limited study in this area.

The scope of this study was to investigate the clarification of waste acid from TiO_2 plants by ceramic MF membranes. Attention was paid to the effect of high concentration $FeSO_4$ and PAA on the filtration process. The influences of other operation parameters such as transmembrane pressure, cross-flow velocity, and TiO_2 concentration on filtration process were also investigated. The study aimed to contribute fundamentally to the design and operation of industrial ceramic MF membrane system for treating titanium white waste acid, in order to recover the TiO_2 and to act as a reliable pretreatment for diffusion dialysis of the waste acid.

2. Experimental

2.1. Membrane

Asymmetric tubular α-Al_2O_3 MF membranes (made in Jiangsu Jiusi High-Tech Co. Ltd., PR China) were used in the filtration experiments. The dimensions of the membranes were 8 mm inner diameter (i.d.), 12 mm outer diameter (o.d.) and 200 mm length. The average membrane thickness was about 30 μm and the surface area per element was 0.005 m^2. The nominal pore sizes used were 0.2 and 0.8 μm. The average pure water flux (PWF) of these membranes were 1200 and 6000 L m^{-2} h^{-1} bar^{-1}, respectively.

2.2. Waste acid

Titanium waste acid was obtained from Nanjing Titanium White Chemical Co. Ltd. The waste acid contained more than 20% (by weight) of sulfuric acid, 200 g L^{-1} of ferrous sulfate and 100 mg L^{-1} of TiO_2 particles.

It should be noted that waste acid were taken directly from the plant before the filtration experiments. Otherwise, different results could be obtained due to the ‘aging’ effects in filtration experiments caused by a variety of undesirable influences such as biological action, chemical reactions, flocculation, etc.

2.3. MF setup

The bench-scale system was constructed of ABS and of stainless steel (SS) and comprised a recirculation loop and a backpulsing arrangement (Fig. 1). The recirculation loop was composed of a 10 L feed tank (jacketed for retentate temperature control), a rotameter, a 2 hp (horse power) centrifugal pump, a membrane module, and the accompanying pressure gauges, valves, and piping. The backpulsing arrangement consisted of a liquid and a gas buffer reservoir and a nitrogen cylinder.

2.4. Analytical procedures

Turbidity of permeate was determined using a HACH 2100N Turbidimeter (HACH, USA). Total suspended solids (TSS) of feed were analyzed using the National Standard Method GB 11901-89 [15].

In some cases, membranes after testing were examined under a JSM-6300 scanning electron microscope (SEM) (JEOL, Japan). The membrane specimens were carefully taken from the middle of the elements (lengthwise) using a pair of pincers and sputter-coated with gold–palladium prior to the SEM analysis.

2.5. Microfiltration runs

Filtration was conducted in constant pressure mode. Before filtration, the PWF values of the membranes were measured to determine the cleanliness and readiness of membranes for testing. During each run, a known volume of the feed solution was processed through the membrane module at a desired transmembrane pressure (TMP) and cross-flow velocity (CFV) (by adjusting valves 1 and 12 in Fig. 1). The feed solution was maintained at a constant concentration by recycling the permeate solution back into the feed tank. The steady flux used in this paper was the permeate flux at the end of 210 min.

After filtration, the ceramic membrane was cleaned with a 0.5 M oxalic acid solution under certain conditions, followed by a thorough rinsing with pure water. The detailed cleaning procedure was described previously [13].

2.6. Analyses of filtration resistances

Analyses of filtration resistances were also done based on a resistance-in-series model using 0.8 μm pore size membranes.

The permeate flux for microfiltration is usually written in terms of transmembrane pressure (TMP) and a total resistance [16]

$$J = \frac{\Delta P}{\mu R_t} \tag{1}$$

where J is the permeation flux (m s^{-1}), ΔP the transmembrane pressure (MPa), R_t the total filtration resistance (m^{-1}), and μ the viscosity of solution (Pa s).

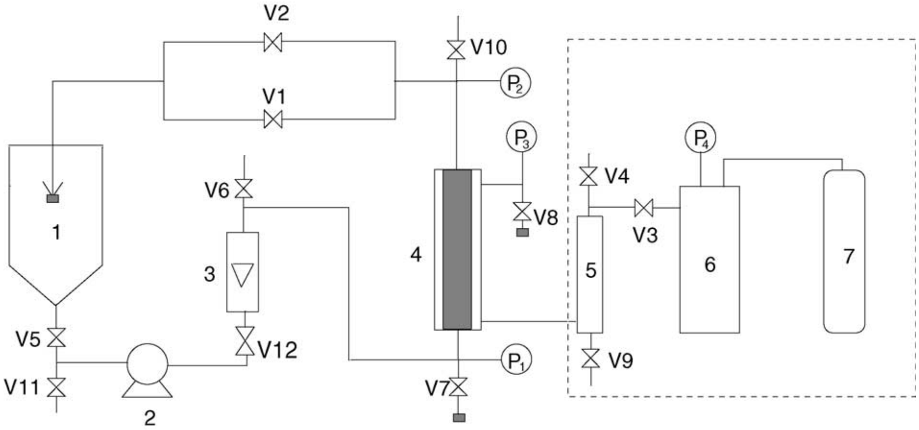

Fig. 1. Schematic diagram of the experimental apparatus. (1) Feed tank, (2) centrifugal pump, (3) rotameter, (4) membrane module, (5) liquid buffer reservoir, (6) gas buffer reservoir and (7) N_2 cylinder. P_1, P_2, P_3 pressure gauges, V1–V12 valves (■), sampling port.

Because the system treated contain micron and submicron-meter particles, the R_t was defined as $R_t = R_m + R_c + R_p + R_i$.

R_m, resistance of the new membrane, can be calculated using pure water flux. R_p, resistance of the polarization layer results from the concentration polarization, can be removed by rinsing with water at very low flow rate. R_c, the resistance of the cake layer results from the deposition of particles and other solute on the membrane surface, which can be removed by brushing the membrane surface. R_i, the resistance due to internal fouling results from the plugging of the fine particles in membrane pores, can be removed chemical cleaning combine with back-flushing.

Experimentally, the resistances defined could be determined from the value of flux in four different periods. First, pure water flux (J_{w1}) was determined using a clean membrane, and then the flux (J_v) of filtration of waste acid was measured. After the filtration of waste acid, the membrane was firstly rinsed with pure water to eliminate all traces of the solution. The rinsing was to remove the polarization layer and the water flux measured afterwards was J_{w2}. The next step was cleaning of the membrane with a suitable brush, followed by rinsing with pure water. This cleaning was to remove the deposited cake and the water flux measured afterwards was J_{w3}.

For filtration resistances experiment, the temperature was fixed at 40 °C. The TMP were 0.06, 0.1, 0.17, 0.25 MPa, the CFV were 1.5, 3.6, 6.5, 9.5 m s^{-1} and the suspension concentration were 0.1, 1, 4 g L^{-1}, respectively.

3. Results and discussion

3.1. Effect of membrane pore size on filtration

The variations of permeate flux and permeate turbidity as a function of time using two pore size membranes are shown in Figs. 2 and 3, respectively.

As shown in Fig. 2, the permeate flux of 0.8 μm pore size membranes was larger than that of 0.2 μm pore size membranes. The difference of the permeate flux might be due to the different characteristic of the cake formed on the membrane. From the selective particle deposition point of view [17,18], critical cut-diameter of deposited particles in a cross-flow filtration depends on the permeate flux under the same cross-flow velocity. The initial flux of 0.8 μm pore size membranes was larger than that of 0.2 μm pore size membranes, so the particle size of cake that formed on 0.8 μm pore size membranes surface might be larger and the cake resistance was smaller than that of 0.2 μm pore size membranes. On the other hand, discrepancy between membrane resistances (R_m) that caused by the pore size of membranes also influences the filtrate flux. As shown in Fig. 2, it could be also found that the flux of 0.8 μm pore size membranes dropped faster from its initial water flux compared with the 0.2 μm pore size membranes. This might be due to the quicker deposition of particles on the larger membrane pore caused

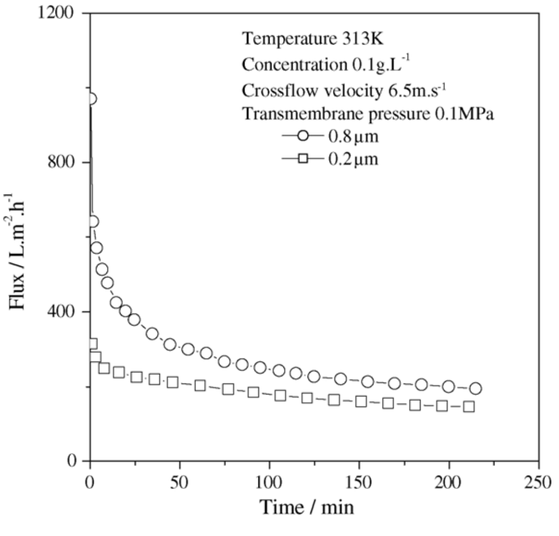

Fig. 2. Variations of permeate flux with time using two pore size membranes.

by the higher initial flux, according to the critical flux theory [19–21].

Good rejection rates were obtained as can be seen in Fig. 3. Although the permeate turbidity of 0.8 μm pore size membranes was slight higher than that of 0.2 μm pore size membranes at the initial stage, the two pore size membranes reached the same steady value of below 0.5NTU at the end of the test runs. This was due to the formation of cake on the membrane, which further improved the rejection rate.

With its higher permeate flux and excellent clarification effect, the 0.8 μm pore size membranes are considered more suitable than the 0.2 μm pore size membranes for pretreating the waste acid before diffusion dialysis.

3.2. *Effect of temperature and high concentration $FeSO_4$*

Temperature is an important factor that affects the permeate flux of membranes. As shown in Fig. 4, the steady flux increased when the temperature was higher than 20 °C. Increase of flux with temperature showed good consistency with the decrease of viscosity of the permeate in this temperature range. This means that the increase of flux with temperature was due to the decrease in viscosity of solutions. Such relationship could be derived from Eq. (1).

With regard to the waste acid, the effect of temperature on solubility of the $FeSO_4$ should also be considered. First, filtration of waste acid was carried out at 50 °C for 210 min. Then, the temperature was decreased step-by-step to 40, 31, 23 and below 20 °C for about 120 min, respectively. The variation of permeate flux with decreasing temperature step-by-step is shown in Fig. 5.

As shown in Fig. 5, the flux decreased with decrease of temperature. When the temperature was below 20 °C, the flux decreased sharply and gradually reduced toward zero flux. At the same time, turbidity of the retained waste acid increased remarkably and crystallization of $FeSO_4$ was found. Apparently, crystallization of $FeSO_4$ due to the decrease of temperature had caused severe membrane fouling. Solubility data [22] confirms that the $FeSO_4$ in the waste acid will crystallize at a temperature of below 20 °C.

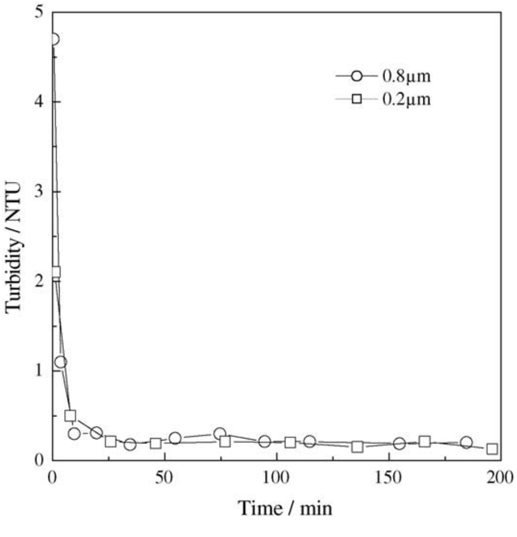

Fig. 3. Variations of permeate turbidity with time using two pore size membranes.

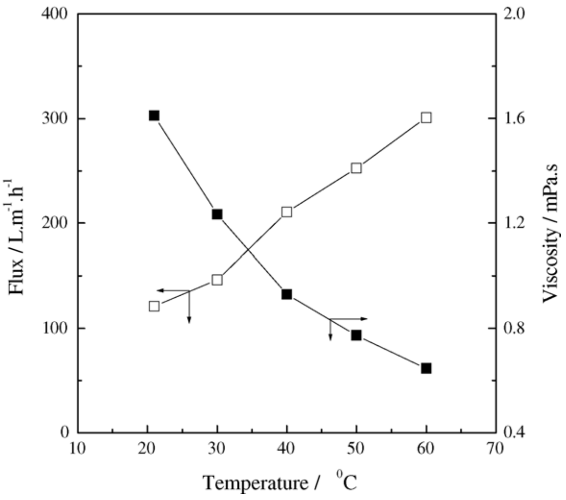

Fig. 4. Effect of temperature on steady-state flux and permeate viscosity.

S.E.M. analysis was carried out to investigate the microstructure of the fouled membrane. As shown in Fig. 6(a), a dense fouling layer composed of very fine crystals was formed on the membrane surface. Fig. 6(b) shows that the crystallization also occurred in the membrane pores and supports. It could be concluded that the crystallization of $FeSO_4$ in membranes and supports plugged the membrane pores, hence reduced the membrane flux seriously.

Repeated experiments showed that the plugged membrane could not be regenerated using hot water and cleaning agent even after a long cleaning time. This may be due to a very low dissolving velocity of the $FeSO_4$ crystal in the microsize pores of the membrane. Therefore, it is very important to maintain a high operating temperature during the filtration

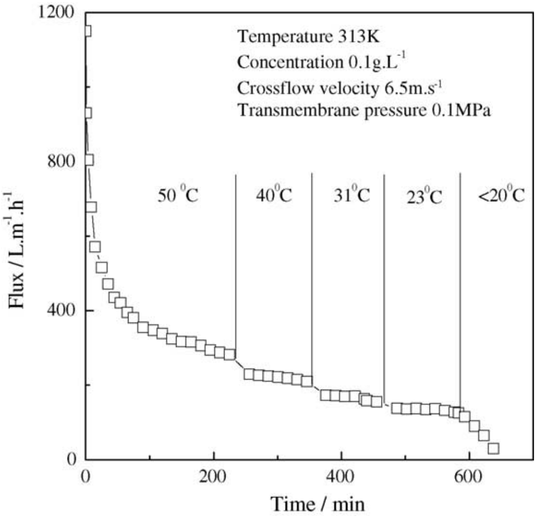

Fig. 5. Variation of permeate flux with temperature.

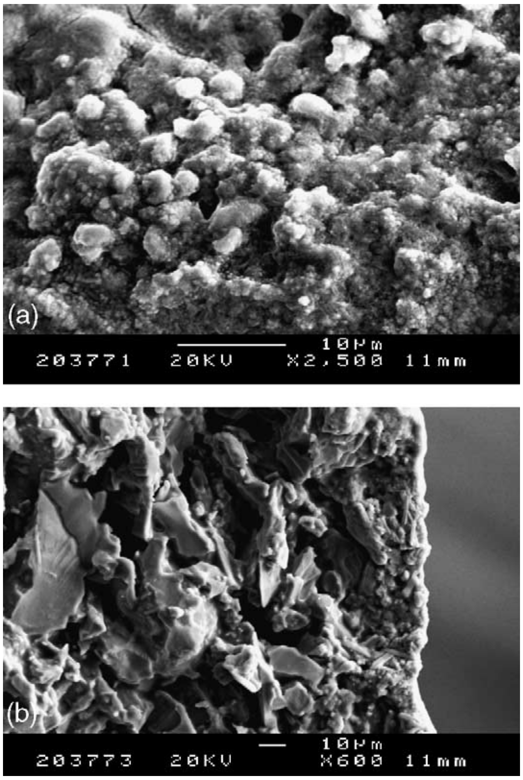

Fig. 6. SEM photographs of the plugged membrane: (a) surface; (b) cross-section.

process, which will not only increase the permeate flux, but also prolong the lifespan of the membrane.

3.3. *Effect of flocculant of PAA*

During settling process, modified polyacrylamide (m-PAA) is always added into mother solutions for speeding the settlement of particles, some residual m-PAA may remain in the waste acid. To investigate the effect of m-PAA on the filtration, experiments were carried out with two types of waste acid, one of which contained m-PAA (about 1 ppm as per in the actual plant), while the other contained no m-PAA. After 3 h of filtration, additional m-PAA was added into the m-PAA containing waste acid to investigate the effect of increasing PAA concentration on the filtration. The results are shown in Fig. 7.

As shown in Fig. 7, the permeate flux was higher for waste acid containing m-PAA than the waste acid without m-PAA. This might be due to the flocculation effects of m-PAA, which lead to the formation of larger flocs thus producing a more permeable cake. However, when the concentration of m-PAA exceeded 5 ppm, the permeate flux decreased. This could be due to the adsorption of m-PAA on the ceramic membrane. The m-PAA used in experiment was a modified negatively charged flocculant. The ceramic membranes used had a positive zeta potential and were positively charged in the acid environment, which was present. Besides being adsorbed onto TiO_2 particles in the waste acid, the remaining m-PAA might also be adsorbed onto the ceramic membrane, resulting an increase in membrane resistance and decrease in the permeate flux.

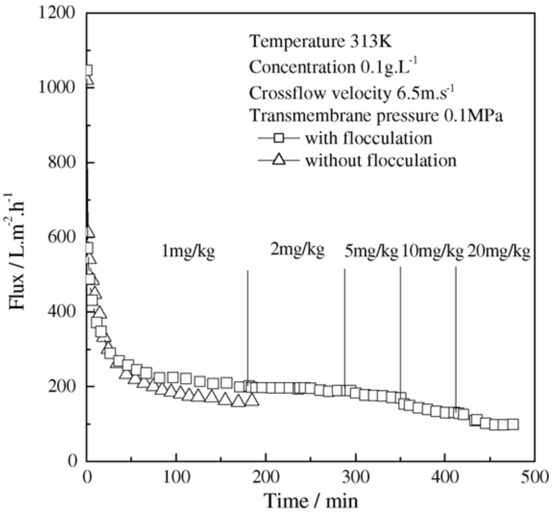

Fig. 7. Effect of flocculants on membrane filtration.

Based on these results, controlling an appropriate amount of flocculant in the waste acid is necessary to improve the filtration in practical application, otherwise the flocculant may cause an increase in the membrane fouling rather than an improvement in the permeate flux.

3.4. *Effects of other operating parameters*

Effects of other operating parameters such as transmembrane pressure, cross-flow velocity and suspension concentration on the steady flux at 40 °C are shown in Figs. 8–10, respectively.

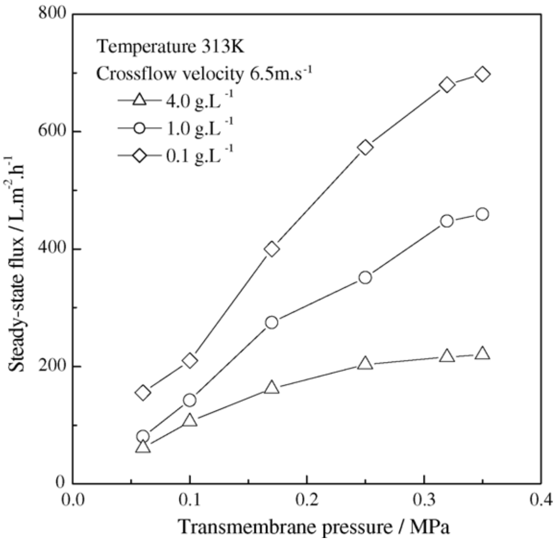

Fig. 8. Effect of transmembrane pressure on steady flux under different concentrations.

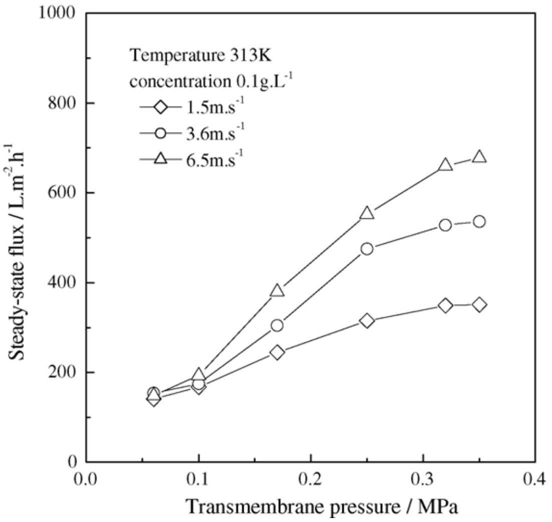

Fig. 9. Effect of transmembrane pressure on steady flux under different velocities.

As shown in Figs. 8 and 9, the membrane flux increased with the transmembrane pressure. However, the effect of transmembrane pressure on the flux was affected by cross-flow velocity and suspension concentration. Increase of the flux with transmembrane pressure was more significant at high velocity and low suspension concentration. This might be due to the formation of thicker cake layer on the surface of the membrane at low velocity and high suspension concentration. On the other hand, an increase of the transmembrane pressure would result in more cake resistance due to compression of cake, which then counteracts the positive effect of the transmembrane pressure on the flux. Therefore, the increase of permeate flux at low velocity and high concentration was less significant.

Generally, an increase of cross-flow velocity will produce a higher flux because the increase of cross-flow velocity leads to an increase of shear stress, which promotes the efficient removal of particles of the dynamic layer deposited on the membrane surface. The effect of cross-flow velocity is shown in Fig. 10. The effect of cross-flow velocity on the flux varied under different suspension concentrations. At 4 g L^{-1} of suspension, the steady flux increased linearly with cross-flow velocity as expected. However, the positive influence of cross-flow velocity on the flux was weakened at low suspension concentrations. At 0.1 g L^{-1} of suspension, the permeate flux slightly increased with cross-flow velocity in the range of 1.5–6.5 m s^{-1}, the trend reversed when the cross-flow velocity increased further than 6.5 m s^{-1}. The latter trend was also observed in literature [23] on polymeric membranes.

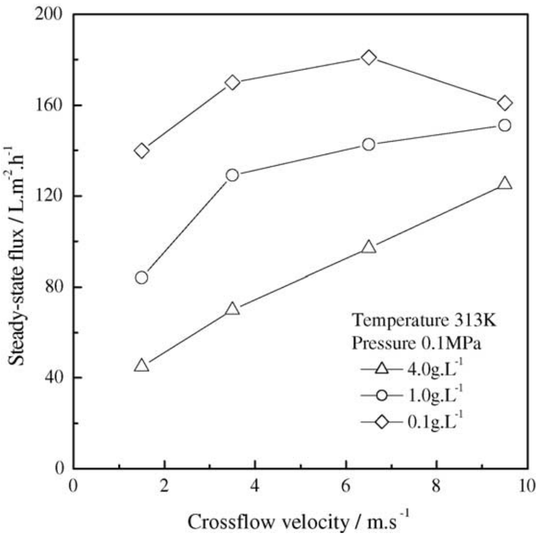

Fig. 10. Effect of cross-flow velocity on steady flux under different suspension concentrations.

To explain the phenomenon, a term for particle classification near the membrane surface [17,18] might be considered. Besides the positive influence of cake decrease on the filtration, increasing cross-flow velocity might cause the particles of cake formed on the membrane to become finer as larger particles are removed from the fouling layer by the scouring action of the cross-flow stream, which would produce a negative influence on the filtration. Hence, two competing factors may contribute to the effect of the cross-flow velocity on the flux. The following hypothesis was derived. At high suspension concentration and low cross-flow velocity ranges, when a thicker cake layer was formed on the membrane, the decrease of the cake layer by the increasing cross-flow velocity might be a controlling factor for the increase of permeate flux. At low suspension concentration and high velocity ranges, however, the thinner cake layer formed on the membrane weakens the positive influence of cake decrease and the particle classification of cake became the dominated factor. As a result, the steady flux decreased with the cross-flow velocity in the range of higher velocity and low suspension concentration.

As can be seen from Figs. 8 and 10, an increase in suspension concentration resulted in a decrease in steady flux. This was a consequence of enhancements of concentration polarization and deposition of particles, which increased the filtration resistance.

It could be concluded that effects of operating parameters such as transmembrane pressure, cross-flow velocity and concentration on the filtration are interrelated and these factors interact on each other. Such characteristic should be considered in the filtration operation. Therefore, in pilot and industrial applications, the transmembrane pressure and cross-flow velocity should be no more than 0.25 MPa and 6.5 m s^{-1}, respectively, at a concentration of less than 4 g L^{-1}.

3.5. *Effect of operating parameters on the filtration resistances*

The resistance and their relative percentages as a function of TMP, CFV, and concentration are shown in Tables 1–3.

As shown in Tables 1–3, R_c was the main component of the fouling resistances and was 68–80% of R_t. R_p was 7.5–10.5% and R_i was 9–18% of R_t. R_m was negligible compared with the fouling resistances, which was only 2–5% of R_t.

Table 1
Hydraulic resistance and relative percentage as a function of pressure (cross-flow velocity 6.5 m s^{-1}, concentration 0.1 g L^{-1})

Pressure (MPa)	R_t		R_c		R_i		R_p		R_m	
	10^{11} m^{-1}	%	10^{11} m^{-1}	%	10^{11} m^{-1}	%	10^{11} m^{-1}	%	10^{11} m^{-1}	%
0.06	19.06	100	13.08	68.58	3.36	17.64	1.72	9.04	0.90	4.74
0.10	19.97	100	13.84	69.30	3.44	17.20	1.78	8.96	0.91	4.54
0.17	24.30	100	17.50	72.00	3.76	15.45	2.16	8.90	0.89	3.65
0.25	31.25	100	23.64	75.66	3.81	12.19	2.91	9.31	0.89	2.84

Table 2
Hydraulic resistance and relative percentage as a function of cross-flow velocity (transmembrane pressure 0.1 MPa, concentration 0.1 g L^{-1})

Velocity (m s^{-1})	R_t		R_c		R_i		R_p		R_m	
	10^{11} m^{-1}	%	10^{11} m^{-1}	%	10^{11} m^{-1}	%	10^{11} m^{-1}	%	10^{11} m^{-1}	%
1.5	27.48	100	20.46	74.47	3.33	12.13	2.78	10.10	0.91	3.30
3.6	22.79	100	16.52	72.46	3.41	14.95	1.97	8.63	0.90	3.96
6.5	19.97	100	13.93	69.76	3.44	17.20	1.70	8.49	0.91	4.54
9.5	20.94	100	14.80	70.66	3.66	17.48	1.58	7.55	0.90	4.31

Table 3
Hydraulic resistance and relative percentage as a function of suspension concentration (transmembrane pressure 0.1 MPa, cross-flow velocity 6.5 m s^{-1})

Concentration (g L^{-1})	R_t		R_c		R_i		R_p		R_m	
	10^{11} m^{-1}	%	10^{11} m^{-1}	%	10^{11} m^{-1}	%	10^{11} m^{-1}	%	10^{11} m^{-1}	%
0.1	19.97	100	13.93	69.76	3.44	17.20	1.70	8.50	0.91	4.54
1.0	27.10	100	20.31	74.96	3.66	13.51	2.22	8.20	0.90	3.33
4.0	39.95	100	32.24	80.71	3.79	9.48	3.02	7.55	0.90	2.26

It could be found that R_t increased significantly with increasing TMP. Among the total resistance, R_c increased significantly with increasing TMP while R_p and R_i increased slightly. An increase of TMP could enhance the convective flow of particle towards the membrane, which subsequently enhances the polarization and deposition of particle. This explained the change of R_c and R_p with pressure. Due to the increase of fouling resistance with pressure, the degree of increase of filtrate flux was lower than that of pure water flux. This confirmed the results obtained in Section 3.4.

R_t and R_c decreased with CFV within the low velocity range of less than 6.5 m s^{-1} and then increased at the high range. R_p decreased with increasing CFV while R_i increased slightly. The decrease of R_p was due to the thinner diffusion layer caused by the increase of CFV. This influence would be due to its role in the shearing stress. Meanwhile the deposit layer would also become thinner. This was the positive influence of velocity on the filtration. On the other hand, increase of CFV would cause the particles of cake formed becoming finer due to the selective deposition of particles caused by cross-flow effect and produce a negative influence on the filtration [17]. Thus two competing factors may contribute to the change of R_c with the increase of velocity. This confirmed the hypothesis in Section 3.4 about the effect of cross-flow velocity on the filtration flux.

It is well known that increase of concentration will enhance the concentration polarization and deposition of particles, which result in the increase of R_c and R_p, as shown in Table 3. The increase of R_c was attributed to the increase of cake mass, and increase of R_i may due to the increase of the number of finer particles. However, the percentage of R_i decreased with the concentration while the percentage of R_c increased as shown in Table 3. It could be concluded that influence of concentration on cake fouling was more remarkable, which is consistent with the results obtained in Section 3.4.

4. Conclusions

Hydrated TiO_2 in titanium white waste acid can be successfully removed using 0.8 μm pore size ceramic membranes and an excellent clarification effect was achieved. The turbidity of clarified waste acid was less than 0.5NTU. The technology is reliable for the pretreatment of the waste acid before the diffusion dialysis.

High concentrations of $FeSO_4$ complicated the effect of temperature on filtration process. When the temperature decreased to less than 293 K, crystallization of $FeSO_4$ might occur in the membrane which caused the permeate flux to decrease toward zero and the membrane could not be regenerated. Maintaining a higher temperature is therefore very important for the filtration process.

Flocculation by modified polyacrylamide, of which the concentration was less than 5 ppm, increased the membrane flux. Further addition of flocculants might cause adsorption fouling of the membrane and resulted in a decrease of the flux.

The membrane flux was also affected by other parameters. The influences of operating parameters, including transmembrane pressure, cross-flow velocity and suspension concentration were interrelated and these factors interacted on each other. Therefore, in pilot and industrial applications, the transmembrane pressure and cross-flow velocity should be kept below 0.25 MPa and $6.5\,\mathrm{m\,s^{-1}}$, respectively, when the suspension concentration is less than $4\,\mathrm{g\,L^{-1}}$.

Analyses of filtration resistances were also done and the results show that the total filtration resistance (R_t) was composed of the cake resistance (R_c), the polarization layer resistance (R_p), the internal plugging resistance (R_i) and the membranes own resistance (R_m). R_c was the main component of the fouling resistances and was 68–80% of R_t. R_p was 7.5–10.5% and R_i was 9–18% of R_t. R_m was negligible compared with the fouling resistances, which was only 2–5% of R_t. The results added more quantitative understanding into the effects of the operating parameters on the filtration.

Acknowledgements

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